Temperature and Potential Scan Rate Effects on Critical Pitting Potentials in Brines

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Abstract

Electrochemical corrosion tests are ongoing at the Lawrence Livermore National Laboratory to assist in the selection of suitable metallic materials to contain spent nuclear fuel and vitrified high-level nuclear waste for geologic disposal in the potential Yucca Mountain repository. Although the groundwater in the vicinity of the potential repository is believed to be non-aggressive for many corrosion-resistant alloys, under certain operating conditions the repository environments surrounding the waste packages may become very hostile and cause localized attack such as pitting and crevice corrosion. This paper presents the results of cyclic potentiodynamic polarization (CPP) experiments on three iron-nickel-chromium-molybdenum alloys showing the effects of temperature and potential scan rate on localized corrosion behavior.

Materials tested include Alloys 825, G-3 and G-30. Since the precise environment that will surround the waste packages is unknown, tests were performed in deaerated acidic, neutral and alkaline brines containing 1-10 weight percent (wt%) NaCl at 50°C, 70°C and 90°C. The pH of these salt solutions ranged between 2 and 3, 6 and 7, and 10 and 11, respectively. The rationale for selecting these environments is provided elsewhere.[1]

A three-electrode technique was used to perform CPP tests in a Pyrex cell using a polished cylindrical specimen as working electrode, two graphite counter electrodes, and Luggin capillary connected to a Ag/AgCl reference electrode. Potential was applied to the test specimens at scan rates of 0.043, 0.085, 0.17 and 0.34 mV/sec using EG&G Models 273 and 283 potentiostats, controlled by an IBM-compatible PC with EG&G corrosion software.

Forward potential scans were done in the noble direction commencing at the stable corrosion potential (E_{corr}), and continuing to a potential sufficiently noble to either cause pitting or exhibit pit-like indication prior to reversing the potential scan at the same rate. A clockwise hysteresis loop is traced during reverse scan, indicating the possibility of pitting in susceptible alloys. Two pitting parameters, namely the critical pitting potential (E_{pit}), and the protection potential (E_{prot}) can be determined from these tests. The value of E_{pit} denotes the potential at which current increases abruptly on the forward scan, indicating the possibility of pit initiation. E_{prot} indicates the electrochemical potential at which the current returns to passive values during reverse scan, indicating repassivation of pits. The tested specimens were cleaned, followed by visual and microscopic evaluations to determine the presence or absence of pitting/crevice attack.

Results indicate that all three alloys underwent pitting and crevice corrosion, with Alloy 825 exhibiting the maximum susceptibility. The relationship between E_{pit} and temperature for Alloys 825 and G-3 in acidic brines is shown in Figures 1 and 2, respectively. In general, E_{pit} appears to shift to more active direction with increasing temperature, suggesting that these alloys may become more resistant to pitting at lower temperatures. The temperature dependence of E_{pit} appears to be consistent with that observed by other investigators.[2-5] These results may indicate the possibility of a temperature-induced change in protective properties of the passive film on alloy surface, resulting in a reduction in its resistance to breakdown as temperature is increased.[6,7]

The effect of potential scan rate on E_{pit} for Alloys 825, G-3 and G-30 in 90°C acidic, neutral and alkaline brines containing 10 wt% NaCl is shown in Figures 3-5. It appears from these results that the effect of potential scan rate on E_{pit} may vary with the alloys tested, and it is difficult to justify a general behavior. However, two basic types of E_{pit} response to increasing scan rate may be noticed for the alloy/environment combinations used in this study. The first one is an initial shift in E_{pit} to more noble values with increasing scan rate followed by a shift in the active direction (Figures 3 and 5). A similar shift in E_{pit} in the active direction with increasing scan rate has been reported elsewhere[8], which is in contrast to the observation by Leckie[9] who reported more noble E_{pit} values at faster scan rates. The second type may consist of an initial shift of E_{pit} in the noble direction in response to a faster scan rate followed by subsequent shifts in the active and noble directions, respectively, as shown in Figures 3 and 4. Since an induction time is necessary for pit formation, E_{pit} response to scan rate seems to be a function of the kinetics of passive film formation at applied potentials.

Acknowledgments

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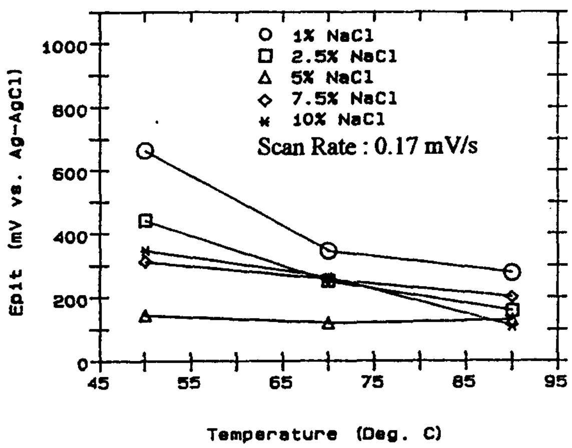

Figure 1. Pitting Potential vs Temperature for Alloy 825 in Acidic Brines

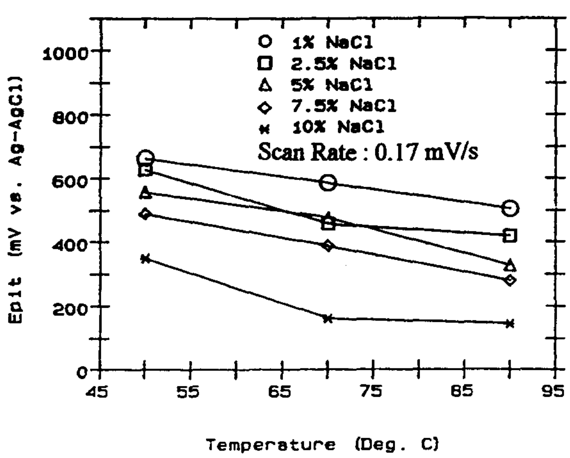

Figure 2. Pitting Potential vs Temperature for Alloy G-3 in Acidic Brines

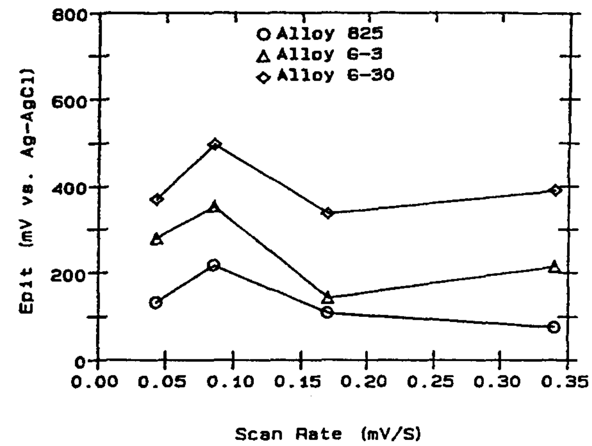

Figure 3. Pitting Potential vs Scan Rate in Acidic Brines Containing 10 wt% NaCl at 90°C

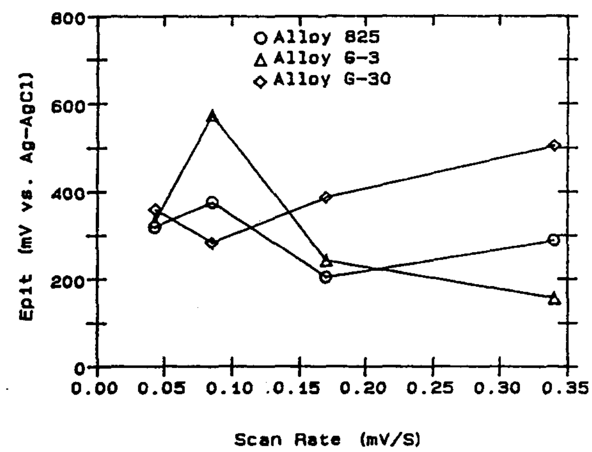

Figure 4. Pitting Potential vs Scan Rate in Neutral Brines Containing 10 wt% NaCl at 90°C

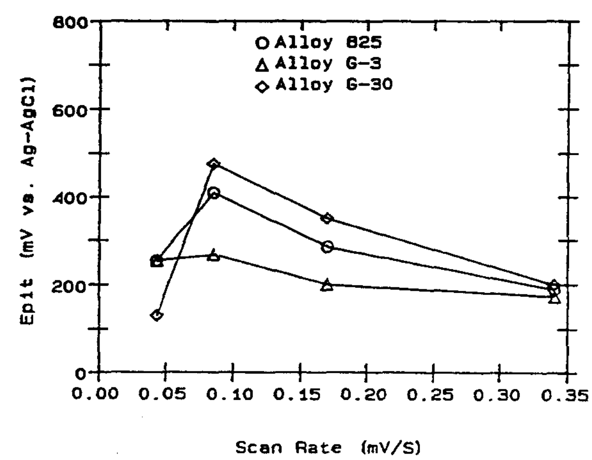

Figure 5. Pitting Potential vs Scan Rate in Alkaline Brines Containing 10 wt% NaCl at 90°C